

Toutes les communications orales ont lieu dans Amphithéâtre Dorothy Hodgkin.

Les pauses café, le buffet de midi et la séance poster ont lieu dans le Hall Emmy Noether

## Programme :

8h45-9h15	Accueil des participants		
9h15-9h30	<b>Introduction</b>	<i>Gilles Grégoire (CPPS), Philippe Maitre (ENS Paris Saclay)</i>	
9h30-10h15	<b>Conférence Plénière:</b> Majed Chergui	<b>EPFL Lausanne</b>	<i>Ultrafast extreme ultraviolet to hard X-ray Pulses as probes of Molecular and Materials Dynamics</i>
10h15-10h35	O1 : Lorenzo Casimiro	<b>PPSM</b>	<i>Azobenzene-based photochromes: exploiting the molecular rearrangements in organic synthesis, optics and molecular machinery</i>
10h35-10h55	Pause café		
10h55-11h05	Patrick Guenoun	PHOM, GS Physique	
11h05-11h35	<b>Keynote 1:</b> Nathanaëlle Schneider	<b>IPVF</b>	<i>ALD-oxide materials and surface modification for next-generation PV devices</i>
11h35-11h55	O2 : Wanlin Chen	<b>LAMBE</b>	<i>On the trail of molecular hydrophilicity and hydrophobicity at aqueous interfaces</i>
11h55-12h15	O3 : Ander Camiruaga	<b>ISMO</b>	<i>Spectroscopic study of intermolecular interactions between mannose and receptor models</i>
12h15-15h00	Repas / Séance Posters : Hall Emmy Noether		
15h00-15h10	Damien Prim	GS Chimie	
15h10-15h30	O4 : Hugo Marroux	<b>LIDYL</b>	<i>Direct observation of sub-natural linewidth structures in the x-ray using attosecond transient absorption</i>
15h30-15h50	O5 : Yue Feng	<b>LPMC</b>	<i>The first lithiation of methylated amorphous silicon</i>
15h50-16h20	<b>Keynote 2:</b> Gérard Baldacchino	<b>LIDYL</b>	<i>Effet de débits de dose extrêmes dans le régime femtoseconde dans l'eau avec des électrons relativistes</i>
16h20-16h40	O6 : Philipp Gotico	<b>I2BC</b>	Controlling Charge Trafficking at an Electron Relay of a Bioinspired Triad
16h40-17h00	O7 : Rika Tandiana	<b>ICP</b>	<i>Multi-level Modelling of Gold Nanoparticles in Various Environments</i>
17h	Prix meilleure affiche "jeune"		



# mezzanine

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4 Amphithéâtre Dorothy Hodgkin

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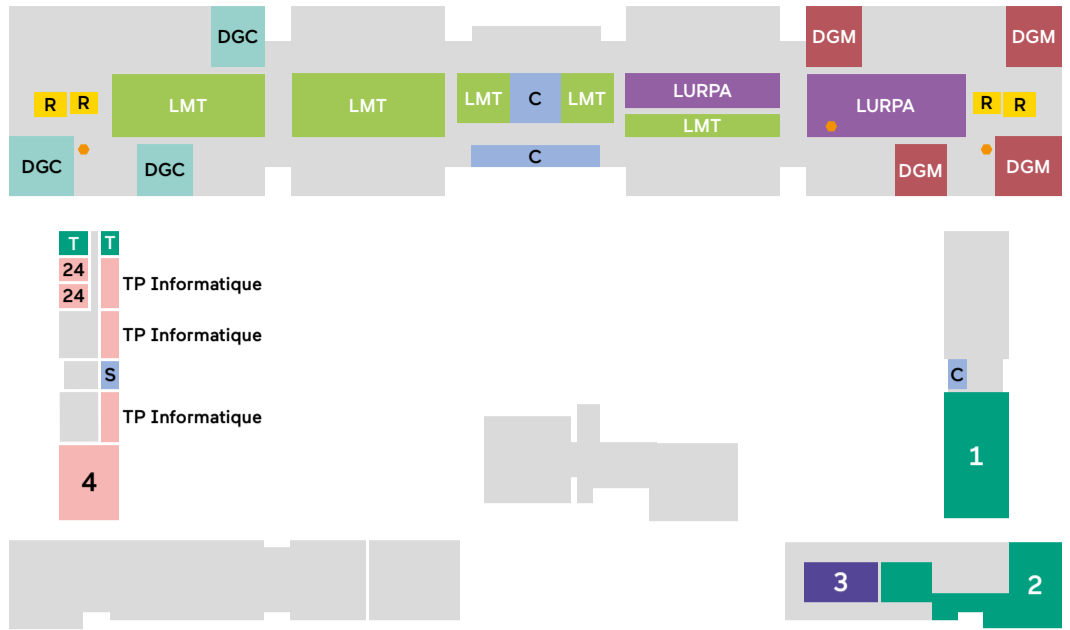
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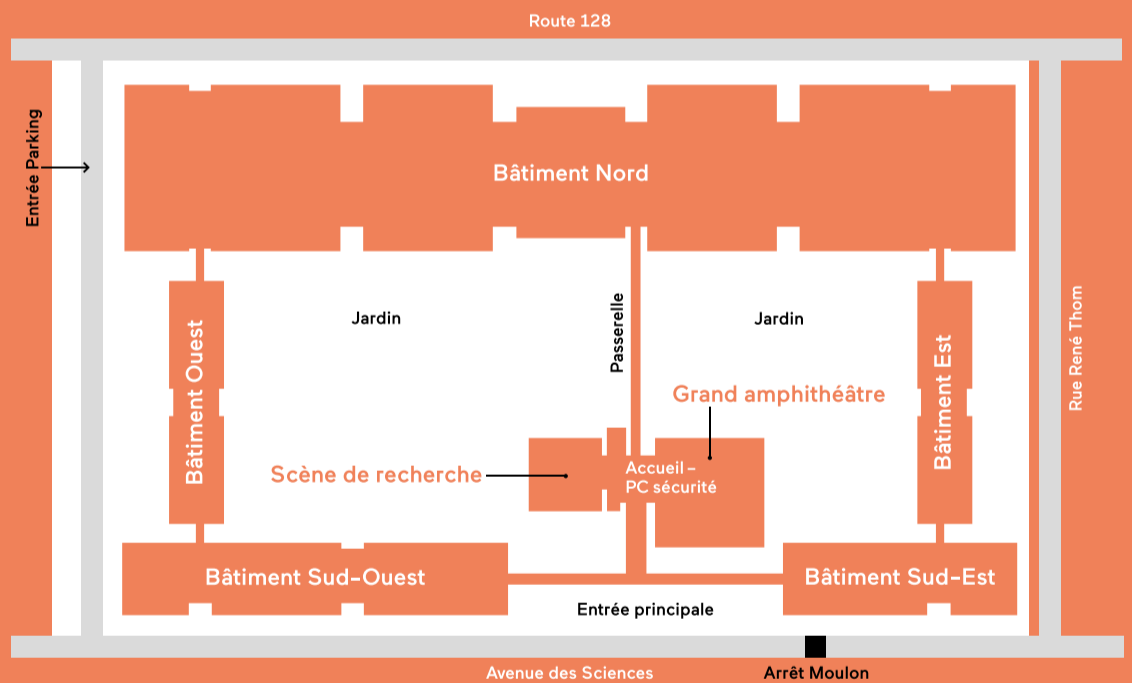


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10 Amphithéâtre Dorothy Hodgkin

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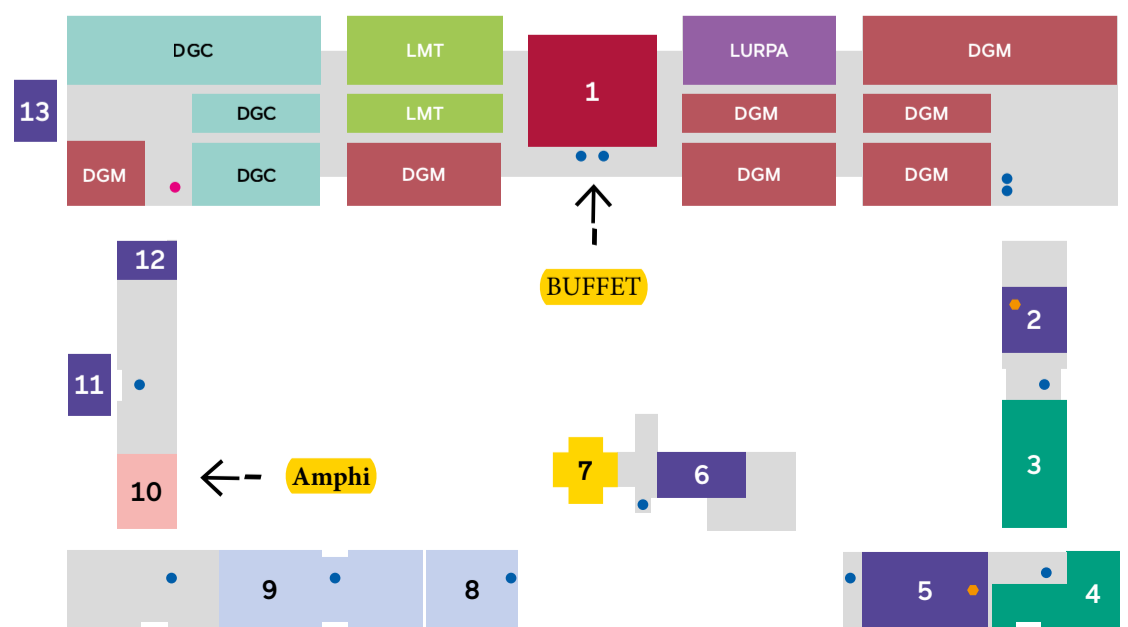
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8 Kfé

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# **Résumés des Oraux**

## Ultrafast extreme ultraviolet to hard X-ray Pulses as probes of Molecular and Materials Dynamics

M. Chergui

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The combination of ultrashort optical and short-wavelength pulses has opened fascinating opportunities for the study of the dynamical behaviour of (bio)chemical systems and of materials. In this respect, the past twenty years have witnessed a revolution in science with the advent of X-ray free electron lasers (XFEL) and table-top high harmonic generation (HHG) sources of short-wavelength radiation. I will show the novel capabilities enabled by XFELs, such as photon-in/photon-out methods (X-ray emission spectroscopy and resonant Inelastic X-ray scattering), or non-linear X-ray optical methods.<sup>1-3</sup> Thereafter, I will present recent results on the study of charge carrier dynamics of perovskites probed by extreme-UV ultrafast angle-resolved photoelectron spectroscopy (fs-ARPES).<sup>4</sup>

### References

- (1) Kinschel, D.; Bacellar, C.; Cannelli, O.; Sorokin, B.; Katayama, T.; Mancini, G. F.; Rouxel, J. R.; Obara, Y.; Nishitani, J.; Ito, H.; Ito, T.; Kurahashi, N.; Higashimura, C.; Kudo, S.; Keane, T.; Lima, F. A.; Gawelda, W.; Zalden, P.; Schulz, S.; Budarz, J. M.; Khakhulin, D.; Galler, A.; Bressler, C.; Milne, C. J.; Penfold, T.; Yabashi, M.; Suzuki, T.; Misawa, K.; Chergui, M. Femtosecond X-Ray Emission Study of the Spin Cross-over Dynamics in Haem Proteins. *Nat. Commun.* **2020**, *11* (1), 4145. <https://doi.org/10.1038/s41467-020-17923-w>.
- (2) Bacellar, C.; Kinschel, D.; Mancini, G. F.; Ingle, R. A.; Rouxel, J.; Cannelli, O.; Cirelli, C.; Knopp, G.; Szlachetko, J.; Lima, F. A.; Menzi, S.; Pamfilidis, G.; Kubicek, K.; Khakhulin, D.; Gawelda, W.; Rodriguez-Fernandez, A.; Biednov, M.; Bressler, C.; Arrell, C. A.; Johnson, P. J. M.; Milne, C. J.; Chergui, M. Spin Cascade and Doming in Ferric Hemes: Femtosecond X-Ray Absorption and X-Ray Emission Studies. *Proc. Natl. Acad. Sci.* **2020**, *117* (36), 21914–21920. <https://doi.org/10.1073/pnas.2009490117>.
- (3) Rouxel, J. R.; Fainozzi, D.; Mankowsky, R.; Rösner, B.; Seniutinas, G.; Mincigrucci, R.; Catalini, S.; Foglia, L.; Cucini, R.; Döring, F.; Kubec, A.; Koch, F.; Bencivenga, F.; Haddad, A. A.; Gessini, A.; Maznev, A. A.; Cirelli, C.; Gerber, S.; Pedrini, B.; Mancini, G. F.; Razzoli, E.; Burian, M.; Ueda, H.; Pamfilidis, G.; Ferrari, E.; Deng, Y.; Mozzanica, A.; Johnson, P. J. M.; Ozerov, D.; Izzo, M. G.; Bottari, C.; Arrell, C.; Divall, E. J.; Zerdane, S.; Sander, M.; Knopp, G.; Beaud, P.; Lemke, H. T.; Milne, C. J.; David, C.; Torre, R.; Chergui, M.; Nelson, K. A.; Masciovecchio, C.; Staub, U.; Patthey, L.; Svetina, C. Hard X-Ray Transient Grating Spectroscopy on Bismuth Germanate. *Nat. Photonics* **2021**, *15* (7), 499–503. <https://doi.org/10.1038/s41566-021-00797-9>.
- (4) Polishchuk, S.; Puppini, M.; Crepaldi, A.; Gatti, G.; Dirin, D. N.; Nazarenko, O.; Colonna, N.; Marzari, N.; Kovalenko, M. V.; Grioni, M.; Chergui, M. Nanoscale-Resolved Surface-to-Bulk Electron Transport in CsPbBr<sub>3</sub> Perovskite. *Nano Lett.* **2022**, *22* (3), 1067–1074. <https://doi.org/10.1021/acs.nanolett.1c03941>.

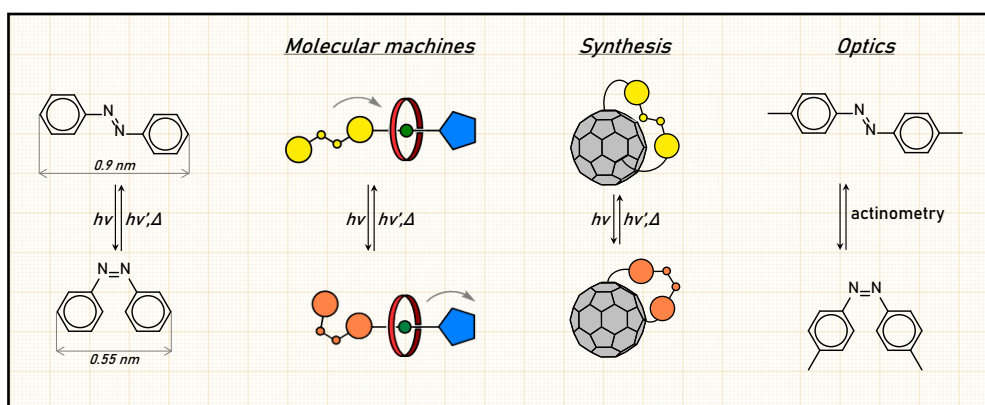
## Azobenzene-based photochromes: exploiting the molecular rearrangements in organic synthesis, optics and molecular machinery

Lorenzo Casimiro,<sup>1</sup> Rémi Métivier,<sup>1</sup> Alberto Credi,<sup>2</sup> Serena Silvi<sup>2</sup>

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Among the plethora of photochromes reported so far, azobenzene derivatives undergo one of the most severe geometrical rearrangements when photoswitched between the *E* and the *Z* forms.<sup>1</sup> We report herewith several ways of exploiting fruitfully such a property. The first use of azobenzene is to rectify the Brownian motion in a supramolecular machine: the photoinduced change in steric hindrance allows a unidirectional pumping of the ring of a pseudorotaxane over the threadlike component.<sup>2</sup> A second example takes advantage of *E/Z* isomerization to change the proximity of two reacting groups and thus to drive the regioselectivity of the cyclopropanation of fullerenes.<sup>3</sup> The last example explores the optical properties of a simple and performant dimethylazobenzene: the photoconversion is efficient and fatigue resistant. After an accurate determination of the quantum yields of photoisomerization, we suggest the use of this molecule as a new and handy chemical actinometer to determine the photon flux of light sources.<sup>4</sup>



### References:

- [1] A. A. Beharry, G. A. Woolley *Chem. Soc. Rev.*, **40**, 4422–4437 (2011)
- [2] G. Ragazzon, M. Baroncini, S. Silvi et al. *Nature Nanotech*, **10**, 70–75 (2015); S. Corra, L. Casimiro, M. Baroncini et al. *Chem. Eur. J.*, **27**, 11076–11083 (2021)
- [3] L. Dordevic, L. Casimiro, N. Demitri et al. *Angew. Chem. Int. Ed.*, **60**, 313–320 (2021)
- [4] L. Casimiro, L. Andreoni, J. Groppi et al. *Photochem. Photobiol. Sci.*, **21**, 825–833 (2022)

## KEYNOTE 1

### ALD-oxide materials and surface modification for next-generation PV devices

Nathanaelle Schneider<sup>1,2</sup>, Damien Coutancier<sup>1,2</sup>, Olivier Fournier<sup>1,3</sup>, Shan-Ting Zhang<sup>1,2</sup>, Martin Foldyna<sup>4</sup>, Muriel Bouttemy<sup>1,5</sup>, François Ozanam<sup>6</sup>, Jean Rousset<sup>1,3</sup>, Polina Volovitch<sup>7</sup>, Jean-François Guillemoles<sup>1,2</sup>

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Photovoltaics are growing rapidly (+30-40% installed volume per year) and is facing many challenges (new usages, 4 to 8 TW capacity by 2050). Hence, academic and industrial communities are developing innovative solar cell architectures involving new materials and interfaces. To build such complicated devices, it is necessary to be able to synthesize nanomaterials with a fine control of the composition, thickness and morphology, under constrained conditions. In this context, ALD (Atomic Layer Deposition) has emerged as a powerful tool because of its unique advantages that I will illustrate by examples on zinc oxide.

This latter is an extensively studied n-type semiconductor for various applications, which often needs to be doped, modified or protected.<sup>[1]</sup> ALD-doped-ZnO films can replace conventional transparent conductive oxides (TCO), especially in high aspect ratio structures. The use of ALD-Ti:ZnO (TZO) as the top electrode for radial junction silicon nanowire (Si NW) based solar cells, has proven ALD unique capabilities, showing superior optoelectrical properties, conformally covering the Si NWs, and yielding a PV diode surpassing the conventional ITO top electrode.<sup>[2]</sup> Modifying the properties of the ZnO surface by grafting organic molecules such as phosphonic acid derivatives is a way to passivate the reactive interface between ALD-ZnO and a hybrid organic inorganic metal halide perovskite.<sup>[3]</sup> Finally, it must be protected to prevent their degradation over the 25 years of utilization. Al:ZnO (AZO) window layer is reported as the primary component responsible for the degradation of CIGS solar cells. While the feasibility to encapsulate module-level (10×10 cm<sup>2</sup>) CIGS solar devices by a 10 nm ALD-Al<sub>2</sub>O<sub>3</sub> barrier layer was demonstrated,<sup>[4]</sup> solar panels in field operation are also exposed to various chemical air pollutants. Their effects were studied and demonstrated the necessity to consider atmospheric chemistry when assessing the durability of PV materials and devices.<sup>[5]</sup>

#### Références

- [1] Z. L. Wang, *J. Phys. Condens. Matter* **2004**, *16*, R829.
- [2] D. Coutancier et al., *ACS Appl. Mater. Interfaces* **2020**, *12*, 21036–21044.
- [3] O. Fournier, et al., *ACS Appl. Energy Mater.* **2021**, *4*, 5787–5797.
- [4] S.-T. Zhang et al., *Sol. Energy Mater. Sol. Cells* **2021**, *222*, 110914.
- [5] S.-T. Zhang et al., *Prog. Photovolt. Res. Appl.* **n.d.**, *n/a*, DOI 10.1002/pip.3527.

## On the trail of molecular hydrophilicity and hydrophobicity at aqueous interfaces

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Understanding from a molecular perspective the organization of liquid water in contact with heterogeneous surfaces as a function of the local surface hydrophilicity is of central importance in many phenomena, ranging from electrochemistry and catalysis<sup>1</sup> to biomolecular recognition<sup>2,3</sup>. Water structure is reorganized at an aqueous interface depending on the balance between water-surface and water-water interactions. Such balance dictates hydrophobicity/hydrophilicity at the molecular level and is subtly related to the nature, the morphology, and the topology of hydrated surfaces. Numerous microscopic descriptors of hydrophobicity/hydrophilicity at interfaces have been developed in the last decades through both MD simulations and surface-sensitive SFG spectroscopy. However, the connections between these theoretical/structural and spectroscopic descriptors are still missing, which limits our fundamental understanding. Here we introduce an original metric to quantify molecular hydrophilicity that bridges the theoretical and spectroscopic fingerprints. We achieved this by studying a platform made of self-assembled monolayers (SAMs) with tunable hydrophobicity and by combining DFT-MD simulations with theoretical and experimental SFG spectroscopy. We define one-to-one relationships between structural motifs at the hydrophilic and hydrophobic interfaces and their specific spectroscopic markers in the SFG spectra. Such markers allow to spectroscopically follow the transition from hydrophilic to hydrophobic environments, they correlate with macroscopic contact angle measurements, and they can reveal even the most subtle changes in the interfacial network. Our metric can be broadly applied to other organic and oxide interfaces, and it can be used to detect local hydrophobicity/-philicity from either qualitative or quantitative interpretation of SFG experiments.

### REFERENCES

- (1) Zhu, J.; Hu, L.; Zhao, P.; Lee, L. Y. S.; Wong, K.-Y. Recent Advances in Electrocatalytic Hydrogen Evolution Using Nanoparticles. *Chem. Rev.* **2019**, *120* (2), 851–918.
- (2) Zhang, L.; Yang, Y.; Kao, Y.-T.; Wang, L.; Zhong, D. Protein Hydration Dynamics and Molecular Mechanism of Coupled Water- Protein Fluctuations. *J. Am. Chem. Soc.* **2009**, *131* (30), 10677–10691.
- (3) Lo Nostro, P.; Ninham, B. W. Hofmeister Phenomena: An Update on Ion Specificity in Biology. *Chem. Rev.* **2012**, *112* (4), 2286–2322.



## Spectroscopic study of intermolecular interactions between mannose and receptor models

Ander Camiruaga<sup>1</sup>, Gildas Goldsztejn<sup>1</sup> and Pierre Çarçabal<sup>1\*</sup>

<sup>1</sup>Institut des Sciences Moléculaires d'Orsay, CNRS, Université Paris Saclay, Orsay, France

Sugars are one of the most important families of biomolecules. They act as mediators of molecular recognition processes. Among the possible biomedical applications, one example is the addition of mannosides to photosensitizers used in PhotoDynamic Therapy, targeting Mannose Receptor (MR) proteins on pathogenic cells. A precise description of the structural basis of Mannose-MR local and direct interplay, which can be provided by gas phase spectroscopy, critically lacks to design PSs with improved selectivity.

In the gas phase, combining experimental mass resolved and conformer selective double resonance vibrational spectroscopy and theoretical chemistry studies, [1] we have already been able to observe several complexes between sugars and peptide models. [2,3] We can now also observe such complexes with a controlled number of water molecules (Figure 1). Our most recent results on complexes of mannose with various peptide models, either hydrated or not, allow resolving the nature of the interactions between the molecules, for each donor and acceptor molecular group involved in the non-covalent bonds governing the complexes. These results reveal the multiple interaction preferences of sugar-peptide complexes. In particular, the study of the complexes formed with few water molecules may highlight the role of water in molecular recognition processes in an unprecedented manner.

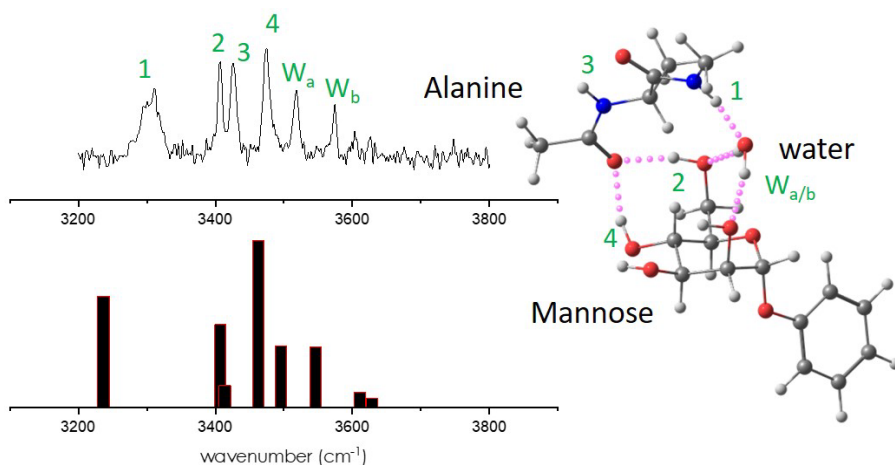


Fig. 1: Experimental (top) and computed (bottom) vibrational spectra of the Alanine-Mannose-water ternary complex.

### Références

- [1] Cocinero E.J.; Çarçabal P., *Top. Curr. Chem.*, 2015, 364, pp. 299-333.
- [2] Cocinero E.J.; Çarçabal P.; Vaden T.D.; Simons J.P.; Davis B.G., *Nature*, 2011, 469, 76-79.
- [3] Cocinero E.J.; Çarçabal P.; Vaden T.D.; Davis B.G.; Simons J.P., *J. Amer. Chem. Soc.*, 2011, 133, 4548-4557.

ORAL 4

**Direct observation of sub-natural linewidth structures in the x-ray using attosecond transient absorption.**

Hugo Marroux

*LIDYL, CEA Saclay*

X-rays are high energy radiations are capable of accessing the core-shell of atoms. This feature provides element specificity to X-ray absorption techniques which is now a tool commonly used in a wide range of fields. The principal limitation of these measurements reside in the short lived excited state created after the absorption of an x-ray photon. These state's few femtosecond lifetimes ( $10^{-15}$  s) broaden the absorption lineshapes hiding fine line structure crucial to understand chemical environment.

We use attosecond ( $10^{-18}$  s) absorption spectroscopy to manipulate the molecular response before the core-excited state decay and obtain sub-natural linewidth information. The line-narrowing behavior is due to a complex light matter coupling we operate using a 3.5 fs pulse. The narrowing reduces the linewidth by a factor up to 7 and is demonstrated on atomic and molecular systems. In the later, our procedure reveals the ligand field splitting of core-level otherwise not accessible directly. This manipulation is only accomplishable because laser sources with short enough pulse duration exist. This approach can potentially be extended to larger molecular target in gas and liquid phases.

## The first lithiation of methylated amorphous silicon

Yue Feng,<sup>1</sup> Abdelhak Cheriet,<sup>1,2,3</sup> Marianthi Panagopoulou,<sup>1</sup> Damien Aureau,<sup>4</sup> Anne Charrier,<sup>5</sup> Alistair C. H. Rowe,<sup>1</sup> Catherine Henry de Villeneuve,<sup>1</sup> Michel Rosso,<sup>1</sup> François Ozanam<sup>1</sup>

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The poor mechanical stability of Si-based anodes during lithiation/delithiation cycles prevents their extensive use in Li-ion batteries. Hydrogenated methylated amorphous silicon (methylated a-Si) thin films exhibit better performance than pure hydrogenated a-Si due to the mechanical softening of the material induced by the introduction of methyl groups into the Si network. The hardness of pure and methylated a-Si with various methyl contents has been investigated using nanoindentation. It confirms that methyl groups induce a softening of the material.

Operando optical microscopy reveals that the first lithiation of a thin film proceeds uniformly over the electrode surface for a-Si layers, but non-uniformly for methylated a-Si layers. [1] The non-uniform lithiation appears to result from an electrostatic instability related to the large resistivity of methylated amorphous silicon. To get rid of the non-homogeneous behavior, boron-doped methylated a-Si has been used since it is more conductive than the undoped material. The first-lithiation behavior turns from inhomogeneous to homogeneous by increasing boron-doping from 0% to 2% in 10% methylated a-Si electrodes. In addition, the material exhibits better electrochemical performance are shown. [2]

The formation of the passivation layer (SEI) on pure and methylated a-Si has been studied by operando infrared spectroscopy. The SEI thickness evolution during the first lithiation/delithiation cycles is found to be similar on pure and methylated a-Si. However, the SEI is richer in lithium carbonate on pure a-Si, whereas it is richer in polycarbonates on methylated a-Si. It is thought to impart flexibility to SEI, which might favor a longer lifetime of methylated a-Si electrodes. A "breathing" behavior is found for the SEI on a-Si, consisting in an apparent increase in the SEI thickness when the electrode is heavily lithiated, and a corresponding decrease during delithiation. The amplitude of this breathing is lower for larger methyl content in the material. Almost no "breathing" is present on methylated a-Si. A more flexible SEI and the absence of "breathing" during cycling could give methylated a-Si a better cyclability.

### Références

[1] Yue et al, *Electrochimica Acta*, **302**, 249-258 (2017)

[2] Yue et al, *Electrochimica Acta*, **403**, 139655 (2022)

## Keynote 2

### **Effet de débits de dose extrêmes dans le régime femtoseconde, dans l'eau avec des électrons relativistes.**

Gérard Baldacchino

*CEA LIDYL (CEA-CNRS-Université Paris Saclay)*

L'intérêt pour les débits de dose élevés de faisceaux d'électrons pour la radiothérapie du cancer (RT) est apparu il y a quelques années avec la découverte de la FLASH RT. Cette nouvelle modalité RT implique des irradiations par des impulsions électrons accélérés des cellules tumorales. La durée des impulsions est alors de l'ordre de la milliseconde. Des impulsions plus courtes provoquant un débit de dose beaucoup plus grand ont été apportées par les nouveaux accélérateurs à plasma laser, qui fournissent des paquets d'électrons de plusieurs dizaines de MeV, avec une durée ultracourte de 100 fs. La question se pose alors de leur pertinence pour la RT. Des investigations par des radiobiologistes ont déjà initiées. Les molécules d'eau étant les principales cibles du corps vivant, il est normal de s'intéresser en priorité aux processus physico-chimiques qui sont engendrées par ces impulsions dans ce milieu. C'est primordial pour comprendre l'impact ultérieur au stade biologique, et éventuellement clinique.

Une étude préliminaire récente que nous avons menée au LIDYL sur la plateforme UHI100 a montré que les rendements radiolytiques des radicaux radio-induits, et en particulier l'électron hydraté, diminuent considérablement contrairement à ceux obtenus avec la même méthode sous des rayonnements conventionnels. C'est la première fois que cela est observé ou que ces rendements sont mesurés, avec ce type d'accélérateur. Nous suggérons d'expliquer cet énorme effet de débit de dose par le fait qu'il se produise avant l'étape de relaxation des états excités. L'effet se traduirait par un taux plus élevé de formation d'eau excitée accompagné de chaleur. On s'attend à ce que l'étape de radiobiologie soit impactée puisque le stress oxydatif est alors diminué. Dans une certaine mesure, ce résultat devrait améliorer l'efficacité de la RT et le confort du patient.

## Controlling Charge Trafficking at an Electron Relay of a Bioinspired Triad

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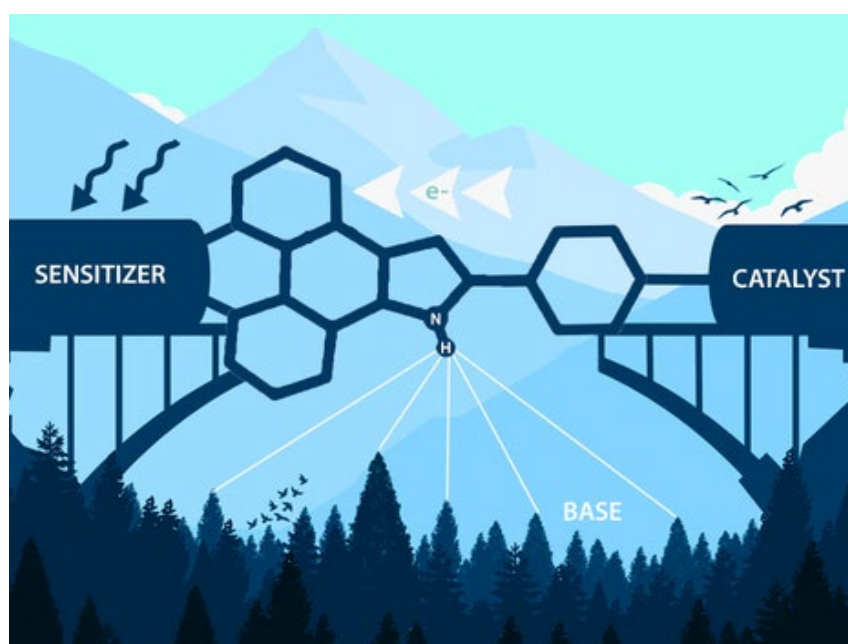
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Electron relays play a crucial role for efficient light-induced activation by a photo-redox moiety of catalysts for multi-electronic transformations. Their insertion between the two units reduces detrimental energy transfer quenching while establishing at the same time unidirectional electron flow. This rectifying function allows charge accumulation necessary for catalysis. Mapping these events in photophysical studies is an important step towards the development of efficient molecular photocatalysts. Three modular complexes comprised of a Ru-chromophore, an imidazole electron relay function, and a terpyridine unit as coordination site for a metal ion were synthesized and the light-induced electron transfer events studied by laser flash photolysis [1]. In all cases, formation of an imidazole radical by internal electron transfer to the oxidized chromophore was observed. The effect of added base evidenced that the reaction sequence depends strongly on the possibility for deprotonation of the imidazole function in a proton-coupled electron transfer process. In the complex with Mn(II) present as a proxy for a catalytic site, a strongly accelerated decay of the imidazole radical together with a decreased rate of back electron transfer from the external electron acceptor to the oxidized complex was observed. This transient formation of an imidazolyl radical is clear evidence for the function of the imidazole group as an electron relay.



[1] P. Gotico, C. Herrero, S. Protti, A. Quaranta, S. Sheth, R. Fallahpour, R. Farran, Z. Halime, M. Sircoglou, A. Aukauloo, W. Leibl, *Photochem Photobiol Sci*, **21**, 247–259 (2022).

## Multi-level Modelling of Gold Nanoparticles in Various Environments

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Gold Nanoparticles (GNPs) have been demonstrated to be promising materials across various research fields, thanks to their tunable chemical, physical, and optical properties. The complexity of GNPs systems can be partly attributed to the dynamic interactions with surface ligands and the solvent. Therefore, with a precise understanding of these dynamic interactions, a rational design of materials with desired properties would be achievable. While various spectroscopic techniques have been widely employed for this effort, computational approaches have been proven to be a powerful method to provide important atomistic insights. Therefore, it is our objective to employ multi-level computational approaches to understand the interaction of GNPs with various environments.

The interfacial interaction of water on a series of increasing size GNP has been systematically probed with classical molecular dynamics and semi-empirical DFTB methodologies.<sup>1</sup> The structural properties of the first solvation shell have been investigated with orientational relaxation lifetime, radial distribution functions, and the distribution of orientations of water molecules. As a result, the re-arrangement of water network to form an extended 2D hydrogen bond network has been observed as the size of GNP increases. The re-arrangement of water network was also confirmed by spectroscopic observations.<sup>2</sup>

In addition to water molecules, the interaction between GNP and surface ligand is important. Therefore, the adsorption of organic molecules on GNP has been systematically investigated at DFT level. Quantum chemical topological analyses have subsequently been performed to identify the formation of multiple non-covalent interactions with varied strength. The energy decomposition analyses were further performed to find that the electrostatic and dispersive interactions were the main contributors to these non-covalent interactions. Vibrational analyses were lastly performed to investigate how the adsorption on GNP affects the IR spectroscopy of the organic compounds. Interestingly, the information on the orientation of the aromatic ring can be deduced from the variation in the intensity of vibrational mode corresponding to the CH stretch of the phenyl ring. This distinct IR signal should be experimentally observable and could help quantify the presence of the various configurations during experiments.<sup>3,4</sup>

### Références

- (1) Tandiana, R., et al., *J. Chem. Phys.* **2021**, *154* (4), 044706.
- (2) Novelli, F., et al., *J. Phys. Chem. B* **2019**, *123* (30), 6521-6528.
- (3) Schunke, C., et al., *Phys. Chem. Chem. Phys.* **2022**, *24* (7), 4485–4492.
- (4) Yao, G., et al., *J. Phys. Chem. C* **2018**, *122* (27), 15241–15251.

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- 2- Julien Audouin, LIDYL : Rendements radiolytiques de  $e^-_{aq}$ ,  $\bullet OH$  et Fricke dans les pics de Bragg de Protons et Carbones dans l'eau
- 3- Valeriu CEMORTAN, LCM: Towards a New Class of Heterometallic Complexes – Synthesis, Characterisation and Theoretical studies
- 4- Lea M. Ibele, ICP: Photochemical reactions in different theoretical representations
- 5- Feven Alemu Korsaye, ENSCP: Density based descriptors for excited state electron density evolution in Real Time - Time Dependent Density Functional Theory
- 6- Karwan Omar, ICP: Does real-time time-dependent density-functional-theory capture peptide ionization by extreme UV pulses?
- 7- Vien-Duong Quach, ICP: Artificial strong metal-support interaction on core-shell nanostructures for photocatalytic and photoelectrochemical enhancement toward hydrogen generation
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- 9- Ewen Lescop, ICSN : Probing the coupled dynamics between lipids and membrane proteins by high-pressure NMR spectroscopy
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15- Gilles Grégoire, ISMO: Spectroscopy and dynamics of NO photodonors

16- Hélène Pasquier, ICP: Assessment of molecular origins of photobleaching of fluorescent proteins

17- Julien Mallétoit, PPSM: Photophysical properties of negative photochromic compounds in solution

18- Salomé Poyer, LAMBE: Complex sulfation pattern observed in glycosaminoglycan sequences deciphered by hydrophilic interaction liquid chromatography-mass spectrometry.

19- Cagla Okyay, LAMBE: Coarse-grained modelling of DNA translocation through a protein nanopore

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# **Résumés des Posters**

## Laser Induced Nucleation in a Microfluidic Mixer for Antisolvent Crystallisation and Precipitation

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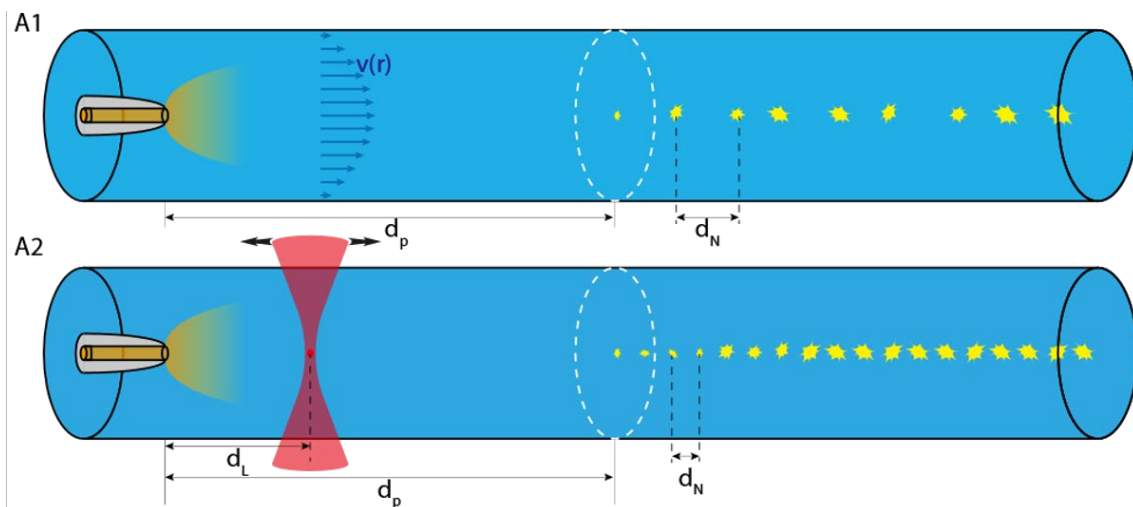
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Non-Photochemical Laser-Induced Nucleation (NPLIN) is an innovative method to trigger or at least accelerate the nucleation in a slow crystallisation process. Microfluidics offers a well-controlled miniature environment for continuous crystallisation. A cosolvent mixer is used to observe the crystallisation and liquid-liquid phase separation of a fluorescent molecule under transmission optical microscopy, birefringence, and fluorescence lifetime imaging microscopy (FLIM). A phase diagram has been measured. Focusing a femtosecond infrared laser in the cosolvent mixer before the spontaneous nucleation starts has increased the nucleation rate by at least one order of magnitudes. The increase of the nucleation rate is observed to be statistically proportional to the laser average power. The polymorphism has not been observed to be apparently influenced by the polarisation of the laser. The laser focal spot has been seen to interact with the interface of the co-flows.



*Schematic illustration of the spontaneous nucleation and the laser induced nucleation in the microfluidic mixer.*

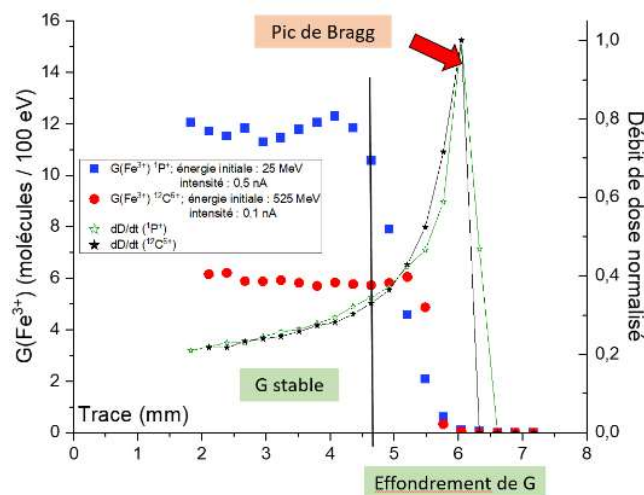
## Rendements radiolytiques de $e^-_{aq}$ , $\bullet OH$ et Fricke dans les pics de Bragg de Protons et Carbones, dans l'eau

Julien Audouin, Gérard Baldacchino

CEA LIDYL (CEA-CNRS-Université Paris Saclay)

Les dépôts d'énergie dans les traces d'ions carbone et proton sont caractérisés en fin de course par un pic de Bragg intense et fin. Cette particularité est exploitée en hadronthérapie pour maximiser la dose délivrée dans la tumeur tout en minimisant celle délivrée dans les tissus sains alentour. Pour comprendre au mieux les phénomènes physico-chimiques se déroulant le long de ces traces, les rendements radiolytiques des espèces résultantes de l'interaction des ions lourds avec l'eau ont été largement étudiés. Mais jusqu'à présent seuls deux types de rendement ont pu être déterminés : les rendements moyens mesurés sur l'intégralité de la trace (incluant le pic de Bragg)<sup>[1]</sup> et les rendements différentiels mesurés sur une portion de la trace où le TEL de l'ion est quasi-constant<sup>[2]</sup>. A notre connaissance aucune détermination de rendements sur les derniers mm d'une trace n'a encore été effectuée. Nous proposons donc de réaliser ces mesures par l'implémentation d'un dispositif original associé à des faisceaux de protons (25, 30 et 62.5 MeV) ou de carbones (525 MeV) fournis par les cyclotrons CEMHTI @Orléans, CAL @Nice et GANIL @Caen.

Nous avons combiné une méthode de capture chimique des radicaux avec la fluorescence pour pouvoir mesurer, en une seule exposition, les rendements de  $e^-_{aq}$  et  $\bullet OH$ . Le rendement du dosimètre de Fricke ( $Fe^{3+}$ ), par absorption à 300 nm, a pu aussi être déterminé par le même dispositif. L'originalité de la méthode repose sur l'utilisation d'un bundle de 20 fibres optiques permettant de mesurer in situ les rendements sur 20 positions différentes avec une résolution de 200  $\mu m$ . Nous comparerons les résultats obtenus avec ceux de la littérature et des simulations.



**Figure :** Rendements de  $Fe^{3+}$  le long de la trace d'un proton de 25 MeV (resp. Carbone de 525 MeV) dans une solution de Fricke. Chaque point correspond à une fibre de 100  $\mu m$  du bundle optique.

### Références

- [1] Smith, M. et al., *Radiat. Phys. Chem.* **188**, 109629 (2021).
- [2] Crumière, F. et al., *Radiochim. Acta* **105**, 487–492 (2017).

## Towards a New Class of Heterometallic Complexes – Synthesis, Characterisation and Theoretical studies

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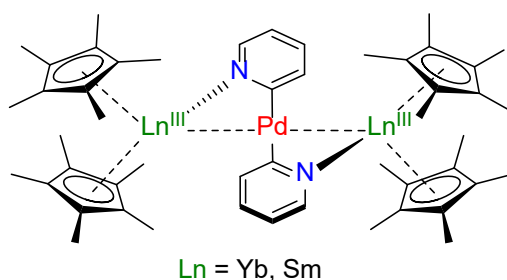
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Since 1965, various divalent lanthanide complexes have been developed<sup>[1]</sup> and display a specific ability to easily transfer one electron.<sup>[2,3]</sup> In association with redox active ligands (RAL) in heterobimetallic complexes, this approach promotes a renewed reactivity of transition metal centers, due to distinctive features of their electronic structures.<sup>[4]</sup> As such, the choice of the RAL has an important influence on the electronic structure of the complex.

Our group has recently explored the use of non-symmetric anionic RALs.<sup>[5]</sup> The addition of organolanthanide fragments of Yb<sup>II</sup> and Sm<sup>II</sup> to a Pd precursor bearing the ligand has yielded unusual isostructural trimetallic complexes (Figure 1) with rare and relatively short Pd-Ln distances (under 3Å), showing a C- activation on the position of the pyridine, accompanied by the departure of the RAL.

Interestingly, the Pd-Ln distances obtained in the solid-state seem to contradict the lanthanide contraction. DFT calculations successfully reproduce the deviation to the expected relative distances between the Yb and Sm trimers. Efforts to explain the formation of these trimers have been undertaken from a mechanistic, spectroscopic and theoretical point of view.

Furthermore, the intermetallic distance is commonly used as an indication of the actual interaction between the metals. An extensive theoretical study has been undertaken to understand this interaction and whether there is a covalent component to it.



**Figure 1** : Structure of trimer complexes

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### References:

- [1] Fischer, E. O.; Fischer, H. *J. Organomet. Chem.* **1965**, **3**, 181-187.
- [2] M. Schultz, J.M. Boncella, D.J. Berg, T.D Tilley, R.A. Andersen. *Organometallics* **2002**, **21(3)**, 460–72.
- [3] G. Nocton, W. W. Lukens, C. H. Booth, S. S. Rozenel, S. A. Medling, L. Maron, R. A. Andersen *J. Am. Chem. Soc.* **2014**, **136**, 8626-8641.
- [4] Chirik, P. J.; Wieghardt, K. *Science*, **2010**, **327**, 794-795.
- [5] D. Wang, M. Tricoire, V. Cemortan, J. Moutet, G. Nocton. *Inorg. Chem. Front.*, **2021**, **8**, 647-657.
- [6] Evans, W. J. *Inorg. Chem.* **2007**, **46 (9)**, 3435–3449.

## POSTER 4

### Photochemical reactions in different theoretical representations

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The Born-Oppenheimer picture has shaped our representation and interpretation of photochemical processes, starting from photoexcitation to the passage through a conical intersection, a funnel connecting different electronic states [1]. While photochemistry in principle contradicts the rationale for the Born-Oppenheimer approximation, a (post-)Born-Oppenheimer formulation has been established as the basis for simulating photochemical experiments, where multiple static potential energy surfaces are coupled together and nuclear amplitudes are propagated on these static surfaces.

Alternatively, the exact factorization provides a point of view, where the concept of multiple time-independent electronic eigenstates disappears, as does the idea that multiple coupled nuclear amplitudes evolve on different static potential energy surfaces [2]. Instead, the exact factorization proposes to represent the dynamics of a molecule in the excited state as a single time-dependent nuclear wavefunction, evolving under the action of a single time-dependent potential energy surface and a single time-dependent vector potential. Concepts, such as conical intersections, transition dipole moment and the molecular Berry phase, do not exist in this formalism.

In this work, I will present how the same photochemical process is represented in the exact factorization and in post Born-Oppenheimer pictures, from the initial explicit excitation by an external laser field to the formation of photoproducts [3]. In most practical simulations of photoprocesses, the dynamics is initialized already on the excited state after the excitation and thus, assuming an infinitely short laser pulse. Here, we study how different explicit descriptions of the initial light absorption process influence the induced relaxation dynamics. In addition to comparing the different representations of photochemistry, I will discuss the different ways in which nuclear trajectories can be employed in both representations to efficiently and accurately describe photochemical reactions [4].

#### Références

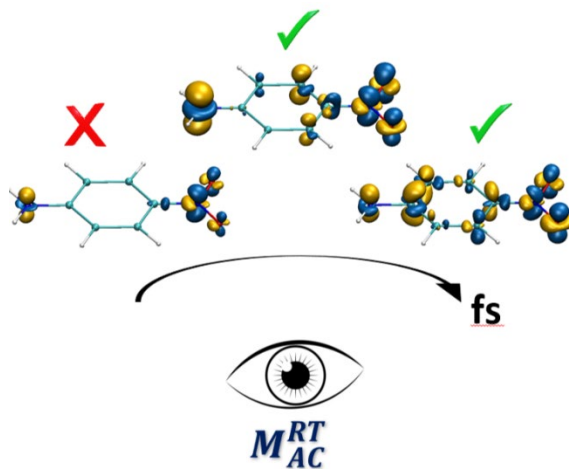
- [1] M. Born and R. Oppenheimer, *Annalen der Physik*, **389**, 457 (1927)
- [2] A. Abedi, N. Maitra and E.K.U. Gross, *Physical Review Letters*, **105**, 23002 (2010)
- [3] L.M. Ibele, B.F.E. Curchod and F. Agostini, *Journal of Physical Chemistry A*, **126**, 1263 (2022)
- [4] F. Agostini and B.F.E. Curchod, *WIREs Computational Molecular Science*, 9:e1417 (2019)

## Density based descriptors for excited state electron density evolution in Real Time - Time Dependent Density Functional Theory

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Density functional theory (DFT) and time-dependent (TD)DFT allow to compute the ground and excited state properties with a simple formalism and a good accuracy to computational cost ratio. Nevertheless, it is well documented in literature the intrinsic drawback of TDDFT theory in modeling the excited states with long-range charge transfer (CT) character. In particular, DFT based approaches fail to reproduce the correct  $1/R$  asymptotic behavior (with  $R$  the distance between the transferred electron and the generated hole) due to the approximated nature of the exchange and correlation functional (XC) used to express the total energy of the system. As

consequence, some of the XC functionals may predict the presence of unphysical states at very low energies and thus providing a misleading picture of the photophysics of the molecules considered [1]. In this scenario the usage of indexes as diagnostic tool to characterize and assess the reliability of TDDFT methods becomes helpful. In particular, the density based DCT index [2] provides for a qualitative measure of the degree of locality of a CT processes by computing the distance of the charge transfer on the basis of the density distribution and the MAC index [3] allows to predict if the excited states obtained at TDDFT level of theory derives from a good or erroneous energy prediction. In this context, with the aim of analyzing the CT states evolution in time we have performed electron dynamics simulations with real-time (RT)TDDFT method. This approach allows to directly propagate the electronic density in time domain enabling to investigate the time-dependent molecular response and modeling the electronic dynamic of excited states in the femtoseconds timescale. In this work the MAC index has been implemented for the RT simulations ( $MAC^{RT}(t)$ ) [4] taking into account the density reorganization during the dynamic and, together with the DCT index, they have been applied to characterize and assess the reliability of excited states dynamics of molecules with CT character in relation to the XC functional used.

### References

- [1] Marco Competella et al. *J. Comput. Chem.*, **38(25)**:2151-2156 (2017)
- [2] Tanguy Le Bahers et al. *J. Chem. Theory Comput.*, **7**:2498–2506 (2011)
- [3] Federica Maschietto et al. *J. Chem. Phys.* **154**:204102 (2021)
- [4] Feven Alemu Korsaye et al. *J. Comput. Chem.*, (2022)

## POSTER 6

### Does real-time time-dependent density-functional-theory capture peptide ionization by extreme UV pulses?

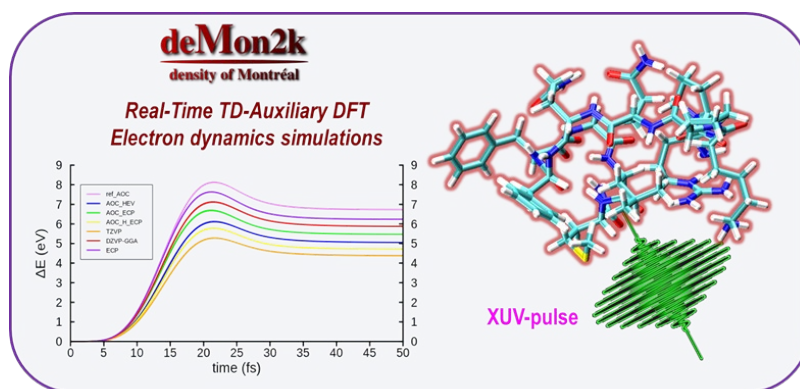
Liste auteur : Karwan OMAR<sup>1</sup>, Fabien CAILLIEZ<sup>1</sup>, Carine CLAVAGUERA<sup>1</sup>, Aurélien DE LA LANDE<sup>1</sup>.

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We are interested in the ultrafast responses of biological molecules to ionizing radiations, for example XUV pulses that lead to excitations and eventually ionization of valence electrons [1]. In order to simulate interaction of XUV-pulse with large molecules, we use real-time time-dependent auxiliary-density-functional theory (RT-TD-ADFT) [2] within the adiabatic approximation as implemented in our local version of deMon2k [3]. We deal with emitted electrons using complex absorbing potentials defined in energy space.

Like most quantum chemistry methods relying on local basis sets (e.g Gaussian functions) that were historically designed for bound states, this kind of methods in principle poorly describes ionization and continuum states. In order to investigate basis set effects, we have benchmarked basis sets on various systems ranging from di-nitrogen to peptides. The systems are irradiated by 30 eV squared cosine shaped pulses with 30 fs duration.

We show that complex absorbing potentials are essential to simulate interaction of XUV with electron emission. We also show that ionization probability essentially relies on the population of ionization states and the symmetry of molecular orbitals associated with the transition energy of XUV. While photo-ionization of small molecules is difficult to describe accurately with Gaussian basis functions using RT-TD-ADFT, difficulties are largely alleviated when larger molecules are considered. Overall, our results are encouraging for future applications of RT-TD-ADFT to interpret attosecond spectroscopy experiments of medium to large size molecules.



#### Références

[1] KA. Omar et al. *Annu Rev Phys Chem*, **72**, 445-465(2021).

[2] A. de la Lande et al. *Theor Chem Acc*, **140**, 126(2021).

[3] A. de la Lande et al. "deMon2k, Version 6," The deMon developers, Cinvestav, Mexico City, 2018.

**Artificial strong metal-support interaction on core-shell nanostructures  
for photocatalytic and photoelectrochemical enhancement  
toward hydrogen generation.**

Vien-Duong Quach<sup>1</sup>, Maria Chiara Spadaro<sup>2</sup>, Marc Botifoll<sup>2</sup>, Jordi Albiol<sup>2</sup>, Mohamed-Nawfal Ghazzal<sup>1\*</sup>)

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Titanium dioxide (TiO<sub>2</sub>) [1] has become one of the most promising and widely studied photocatalyst for a variety of applications, including self-cleaning surfaces, air and water purification systems, advanced oxidation processes, and so forth. In spite of some unique features such as strong oxidation ability, being biologically and chemically inert and non-toxic, TiO<sub>2</sub> photocatalytic capability of harvesting solar light is limited to the UV range due to its large energy bandgap and fast recombination rate of reactive charges [2]. In order to improve its photoactivity, metal doping and non-metal doping strategies were proposed. However, the impurity dopants could initiate defects deeply inside the bandgap structure of TiO<sub>2</sub> that are truly recombination centres for electron-hole pairs, leading to the limited yield of photocatalytic processes. Instead, surface modification or metal nanoparticles coupling has shown great promises on boosting the photocatalytic efficiency in CO<sub>2</sub> reduction, H<sub>2</sub> production, light-driven dry reforming methanation, etc. In general, metal nanoparticles, such as Pt, Au, Cu and Ni are used to collect the photogenerated electrons either to improve e<sup>-</sup>/h<sup>+</sup> lifetime or act as cocatalyst (reduction sites). From a perspective of achieving optimal performance when TiO<sub>2</sub> is coupled with NPs, two prime factors are of pivotal importance: i) the efficiency of electron transfer from TiO<sub>2</sub> to metal nanoparticles active sites and ii) the available reactive surface. For this purpose, mutual metal-support interactions between metal nanoparticles and TiO<sub>2</sub> would offer significant influences on the electronic structure of metal nanoparticles, guarantee an efficient charge transfer, and finally improve the photocatalytic activities.

In this presentation, we reported the construction of artificial “strong metal-support interaction” (SMSI) is well achieved through an elegant soft-chemistry process [3][4]. While a majority of the reports suggested that the SMSI was restricted to metals from group VI, VII and VIII, we proved the possibility of extending to other metal transition in the periodic table, such as Pt, Au, Cu and Ni. In this study, we developed general schemes of synthesizing core@shell nanostructures with metallic nanoparticles - Au, Pt, Cu, Ni - either deposited on outer TiO<sub>2</sub> shell or embedded in inner SiO<sub>2</sub> core and then covered by an overlayer of TiO<sub>2</sub> (shell), thereby studying on strong metal-support interaction (SMSI). Besides, we comprehensively studied and characterized the nanostructures by various aspects, including electrochemistry, photo-electrochemistry, spectroscopy, microscopy, etc, hence pinpoint the behind mechanism for the superior HER and demonstrate that SMSI is more efficient compared to classical system for a variety of metals.

#### Références

- [1] A. FUJISHIMA and K. HONDA, “Electrochemical Photolysis of Water at a Semiconductor Electrode,” *Nature*, vol. 238, no. 5358, pp. 37–38, Jul. 1972, doi: 10.1038/238037a0.
- [2] X. Chen and S. S. Mao, “Titanium dioxide nanomaterials: Synthesis, properties, modifications and applications,” *Chem. Rev.*, vol. 107, no. 7, pp. 2891–2959, 2007, doi: 10.1021/cr0500535.
- [3] G. D. Gesesse *et al.*, “A soft-chemistry assisted strong metal-support interaction on a designed plasmonic core-shell photocatalyst for enhanced photocatalytic hydrogen production,” *Nanoscale*, vol. 12, no. 13, pp. 7011–7023, 2020, doi: 10.1039/C9NR09891G.
- [4] G. D. Gesesse *et al.*, “Plasmonic core-shell nanostructure as an optical photoactive nanolens for enhanced light harvesting and hydrogen production,” *Nanoscale*, vol. 10, no. 43, pp. 20140–20146, 2018, doi: 10.1039/c8nr07475e.



## Spectroscopie du 4(5)-méthylimidazole et de ses hydrates, hébergés en gouttelette d'hélium

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L'histidine est l'un des deux acides aminés qui présente un équilibre tautomérique. Cette molécule est par ailleurs, à la fois accepteur et donneur de proton, ce qui lui donne un rôle essentiel dans les processus biologiques où le transfert d'un proton intervient (ex. régulation du pH sanguin). Des études antérieures ont montré que l'équilibre tautomérique de cet acide aminé est modifié par son environnement<sup>[1]</sup>, ce qui rend ses propriétés intrinsèques délicates à obtenir expérimentalement. Connaître ces propriétés est pourtant important pour comprendre le comportement de cet acide aminé lorsqu'il est environné. Les caractéristiques mentionnées ci-dessus sont uniquement portées par le cycle imidazole qui est la chaîne latérale de l'histidine. Ainsi, nous sommes intéressés à une molécule modèle de l'histidine, le 4(5)-méthylimidazole (Melm) (Figure 1).

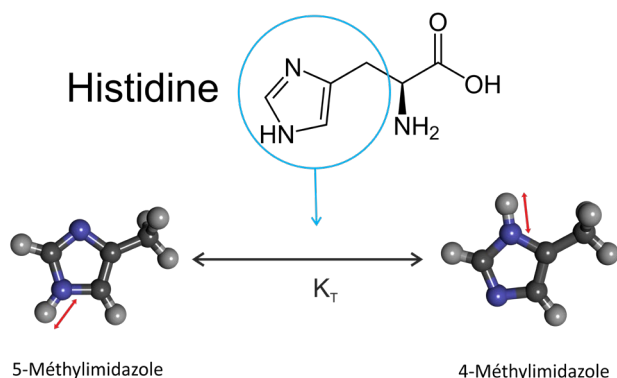


Figure 1: L'histidine et sa molécule modèle, le méthylimidazole.

Sur le plan expérimental, nous avons caractérisé les isomères du Melm et ses hydrates, par spectroscopie infrarouge (IR). Le dispositif Gouttelium<sup>[2]</sup> a permis d'enregistrer les spectres IR de ces espèces en utilisant la technique "Helium NanoDroplet Isolation"<sup>[3]</sup>. Les gouttelettes d'hélium sont des systèmes quantiques froids (0,37 K<sup>[4]</sup>), superfluides<sup>[5]</sup> et très fragiles. Elles thermalisent les espèces qui y sont hébergées et interagissent peu avec ces dernières, ce qui permet d'obtenir des spectres d'absorption IR proche de ceux attendus sur des molécules totalement isolées. Néanmoins, cette observation

porte essentiellement sur la structure vibrationnelle des spectres car la structure rotationnelle est affectée par la présence de la gouttelette.

Nous avons caractérisé sans ambiguïté les deux tautomères du Melm via l'élongation NH dont la fréquence est très sensible à la position du groupe méthyle. L'attribution des bandes IR observées à un conformère spécifique a été faite par comparaison avec des calculs de DFT-D. Les intensités relatives entre bandes nous ont permis d'estimer la constante de tautomérisation,  $K_{5 \leftrightarrow 4}(T=43^\circ\text{C}) = 5,3 \pm 0,8$ , qui n'était pas connue avec précision. Les constantes de rotation du 4-méthylimidazole dans les gouttelettes ont été déterminées grâce à une simulation du spectre et montrent une interaction forte de la rotation avec la gouttelette d'hélium. Ce résultat est attendu car la molécule entraîne une couche d'hélium non superfluide dans sa rotation.

Enfin, les complexes 4(5)-Melm-eau ont été formés par le dépôt des deux espèces dans les gouttelettes d'hélium. Une recherche du signal de l'élongation NH du Melm et de l'élongation symétrique et antisymétrique OH de l'eau a été effectuée.

Les différents spectres et leur interprétation seront présentés, ainsi qu'une discussion.

1. J. A. Vila, *et al.*, *PNAS* **108**, 5602 (2011). <http://dx.doi.org/10.1073/pnas.1102373108>

2. M. Briant, *et al.*, *PCCP* **18**, 16414 (2016). <http://dx.doi.org/10.1039/c6cp02989b>.

3. F. Stienkemeier, *et al.*, *Phys. Rev. Lett.* **74**, 3592 (1995). <http://dx.doi.org/10.1103/PhysRevLett.74.3592>

4. M. Hartmann, *et al.*, *Phys. Rev. Lett.* **75**, 1566 (1995). <http://dx.doi.org/10.1103/PhysRevLett.75.1566>

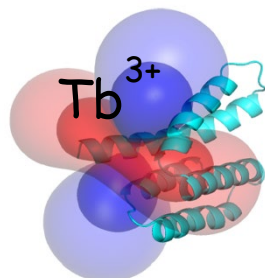
5. M. Hartmann, *et al.*, *Phys. Rev. Lett.* **76**, 4560 (1996). <http://dx.doi.org/10.1103/PhysRevLett.76.4560>

## ParaHP-NMR: Paramagnetic effects under high hydrostatic pressure NMR to probe the structure of proteins and contrast agents.

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The application of hydrostatic high-pressure (HP) is now a recognized tool to modify biomolecular conformational landscapes in a mild and largely reversible manner. HP combined with NMR spectroscopy (HP-NMR) has been extensively used over the years to characterize the folding properties and the dynamics of soluble proteins by stabilizing conformational states that are lowly populated at ambient pressure and characterized by lower partial volumes. On the other side, paramagnetic NMR is a well-established method to probe molecular structures by grafting compounds, such as lanthanides, on proteins and is also central for the development of contrast agents used for MRI. As an example, the Pseudo-Contact Shifts (PCSs) generated by lanthanides such as Yb<sup>3+</sup>, Tb<sup>3+</sup> or Tm<sup>3+</sup> lead to spectral shifts allowing obtaining precise relative positions of the various atoms with respect to the lanthanide probe. Nevertheless, to date, how pressure affects the paramagnetic properties of lanthanides and whether PCS can be used to probe protein structure/dynamics at high pressure is unknown.



Here, we will describe recent progress to assess the pressure effects on PCSs collected on the ubiquitin protein and a contrast agent and we will introduce the paraHP-NMR method. We show that up to 2500 bar, the paramagnetic probes remain chemically intact and that the change in paramagnetic susceptibility tensor is significant but limited. We could detect a small amplitude pressure-dependent conformational deformation at ultra-high precision (a fraction (~1%) of Å !!!). Using Tb<sup>3+</sup> and Tm<sup>3+</sup> grafted at various positions on the ubiquitin protein we could measure by NMR high quality PCSs for backbone <sup>1</sup>H/<sup>1</sup>N atoms from 1 to 2500 bar. We detected a small displacement (~0.5 Å) of the probe from the protein at high pressure and demonstrated that PCSs can be used to probe the structure/dynamics of ubiquitin under high-pressure conditions. Taken together, we established the paramagnetic HP (paraHP-NMR) method as a viable tool to characterize molecular structures under pressure.

## Conversion de spin nucléaire dans les molécules méthylées en matrice de para-hydrogène

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Le para-hydrogène (pH<sub>2</sub>) solide est considéré comme un environnement peu perturbateur pour les molécules qui y sont piégées et en particulier, les mouvements moléculaires de grande amplitude y sont grandement préservés [1]. Nous nous sommes intéressés à la rotation ou la torsion des groupements méthyle qui n'y sont pas bloqués et qui offrent ainsi une observable des effets de faible perturbation par le pH<sub>2</sub>. Pour des raisons de symétrie au sein du groupe CH<sub>3</sub>, les deux premiers niveaux de rotation (K=0 et K=1 sur l'axe C<sub>3v</sub> du groupe méthyle) sont peuplés par des molécules avec les spins nucléaires des H différents : I=3/2 pour K=0 et I=1/2 pour K=1. Les deux niveaux sont peuplés lors de la formation de l'échantillon solide et on peut suivre par spectroscopie IR l'évolution des populations due à la conversion de spin nucléaire (CSN) à 3K sur des temps très longs jusqu'à l'équilibre thermique.

Nous étudions la rotation des méthyles sur des chaînes linéaires méthylées de différentes tailles, à comparer aux travaux antérieurs de Lee et al. [2] sur CH<sub>3</sub>F. De premiers résultats sur le propyne ont mis en évidence des évolutions temporelles importantes dans les spectres IR, attribuées à la CSN. L'ensemble du spectre montre que la rotation d'ensemble du propyne est bloquée ; seule la rotation autour de l'axe C<sub>3v</sub> de la molécule semble préservée dans le pH<sub>2</sub>. Les transitions perpendiculaires liées aux mouvements du méthyle présentent une structure attribuée en partie à la rotation gênée autour de cet axe [3], mais l'attribution publiée n'est pas totalement satisfaisante. Une partie des structures de ces bandes suit une dynamique beaucoup plus lente qui n'a été observée que récemment (voir Figure). Elle pourrait être attribuée à des molécules dont la rotation autour de l'axe C<sub>3v</sub> est suffisamment bloquée pour que le mouvement associé ne soit plus qu'un mouvement de torsion. L'éclatement par effet tunnel des niveaux de torsion produit également des populations de niveaux dépendant du spin des H, et la CSN entre niveaux de torsion peut être suivie dans le pH<sub>2</sub> [4].

L'attribution du spectre propyne/pH<sub>2</sub> est en cours. Nous avons également obtenu des spectres de chaînes méthylées plus longues montrant de nouvelles structures en cours d'analyse.

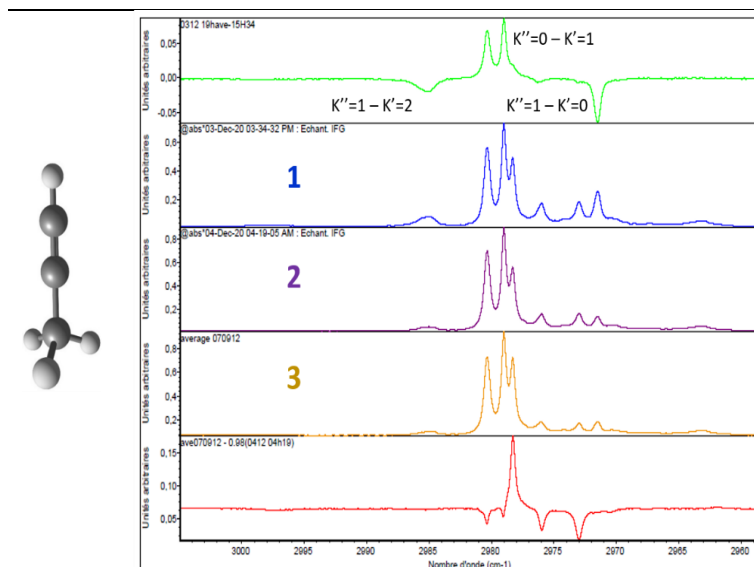


Figure : Bande  $\nu_6$  du propyne (étirement asymétrique des C-H du méthyle) dans pH<sub>2</sub> à 3 K. 1 : spectre 90' après déposition, 2 : 14h après, 3 : 4 jours après (spectre stabilisé à 3K). Haut : spectre de différence 2 – 1 montrant la dynamique « rapide » (200') sur certaines composantes avec leurs attributions ; cela correspond à l'équilibre des populations rotationnelles des molécules ayant une rotation gênée autour de l'axe C<sub>3v</sub>. Bas : spectre de différence 3 – 2 montrant la dynamique « lente » (> 1000') sur les autres composantes ; cela peut correspondre à l'équilibre des populations des molécules ayant une rotation bloquée autour de l'axe C<sub>3v</sub>.

- [1] Gutiérrez-Quintanilla et al., *Faraday Discuss.* **212**, 499 (2018)  
 [2] Lee et al., *J.Chem.Phys.* **129**, 104502 (2008)  
 [3] Strom et al., *J. Phys. Chem. A*, **124**, 22, 4471–4483 (2020)  
 [4] Lozada Garcia et al., *Angewandte Chemie*, **51**, 6947 (2012)

## Évaporation de molécules neutres en fluide supercritique pour une caractérisation structurale par spectroscopie laser résolue en conformation

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L'évaporation d'un échantillon liquide ou solide donne accès à de nombreuses techniques d'analyse (spectrométrie de masse, spectroscopies résolues), et tient une place importante dans l'analyse de molécules biologiques. L'introduction de systèmes neutres en phase gazeuse s'avère toutefois délicate dans le cas de ces molécules fragiles pour lesquelles les techniques existantes (chauffage, désorption par laser) ne conviennent pas toujours. [1]

Dans ce contexte, une nouvelle source comprenant un appareil de chromatographie à fluide supercritique (SFC) utilisant du CO<sub>2</sub> [2] couplé à un jet moléculaire pulsé, a été développée afin d'améliorer un procédé déjà exploré en 2006. [3] Appliquée à des molécules d'intérêt biologique tel que des petits peptides, [4] cette technique a pour objectif de caractériser la structure de systèmes isolés au moyen d'expériences de spectroscopies laser IR et UV résolues en conformation interprétées à l'aide de calculs de chimie quantique. [5]

Les molécules d'intérêt sont dissoutes dans la phase supercritique et acheminées jusqu'à la vanne pulsée qui permet une détente supersonique du mélange sous vide. L'analyse est ensuite réalisée par un spectromètre de masse à temps de vol double (anion/cation) permettant d'enregistrer les spectres résolus en masse.

Les premiers essais ont été menés avec le toluène en solution dans l'éthanol et ont permis de caractériser la source, notamment la stabilité du signal d'ions, la température du jet moléculaire ainsi que les conditions de formation d'agrégats.

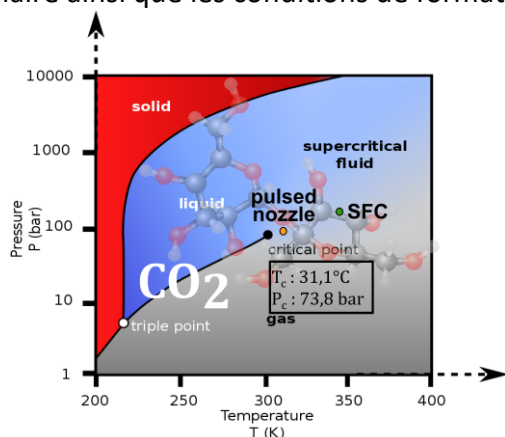


Figure 1 : Diagramme P, T du dioxyde de carbone avec les points de fonctionnement de la SFC (vert) et de la vanne pulsée (jaune).

[1] A. M. Rijs, J. Oomens, *Gas-Phase IR Spectroscopy and Structure of Biological Molecules*, Vol. 364, pp. 1-42 (2015)

[2] C. Chollet et al. *J. Mass Spectrom.*, Vol. 54, pp. 791-801 (2019)

[3] Ishiuchi S.-I., Fujii M, *Chemistry Letters*, Vol. 25, pp. 1044-1045 (2006)

[4] E. Gloaguen, M. Mons, *Gas-Phase IR Spectroscopy and Structure of Biological Molecules*, Vol. 364 (Eds.: A. M. Rijs, J. Oomens), pp. 225-270 (2015)

[5] <https://anr.fr/Projet-ANR-20-CE29-0016>

## Vers un spectromètre 2D-IR à haute résolution

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Claudine Crépin<sup>1</sup>**

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La spectroscopie infrarouge bi-dimensionnelle (2D-IR) est un outil puissant pour explorer la structure et la dynamique de nombreux systèmes. Cette technique de spectroscopie non-linéaire, plus poussée que la spectroscopie d'absorption IR, **permet d'accéder aux informations structurales (anharmonicité, couplage des modes) et dynamiques (transferts d'énergie, diffusion spectrale)**, à des échelles d'une centaine de femtosecondes [1].

Nous avons mis en place un spectromètre 2D-IR permettant l'acquisition de cartes 2D-IR de systèmes moléculaires. Ce **dispositif 2D-IR est polyvalent : combiné à un système cryogénique, il permettra de mener des expériences sur une large gamme de températures, et de sonder des systèmes en solution ou piégés dans des environnements cryogéniques**. La caméra infrarouge multipixel (320x256) apporte une meilleure résolution spectrale ( $<0,5 \text{ cm}^{-1}$ ) que les détecteurs conventionnels [2]. Nous présentons ici des résultats préliminaires sur des petits complexes organométalliques en solution.

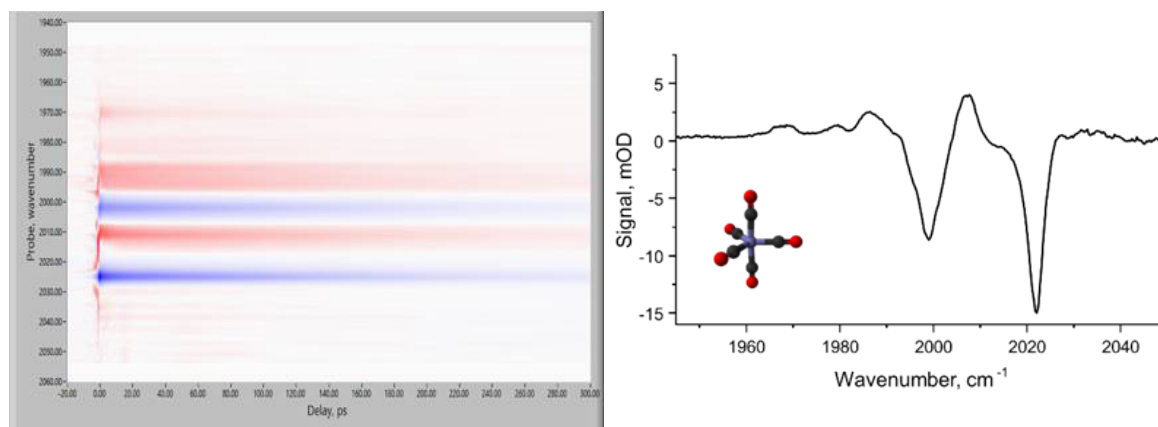


Fig. 1 : A gauche : Signal pompe-sonde du Fe(CO)<sub>5</sub> dans le dodécane mesuré avec la caméra. A droite : spectre d'absorption transitoire correspondant.

[1] Peter Hamm and Martin Zanni, editors. *Concepts and methods of 2D-infrared spectroscopy*. Cambridge University Press, 1. edition, (2011)

[2] Ghosh, A. et al. *Opt. Lett.*, **41**, 524-527, (2016)

\* Affiliation actuelle : LOB, Ecole Polytechnique, IPP, Palaiseau.

## Observation et caractérisation des ions Chlorophylles et Phéophytines par la spectrométrie de masse

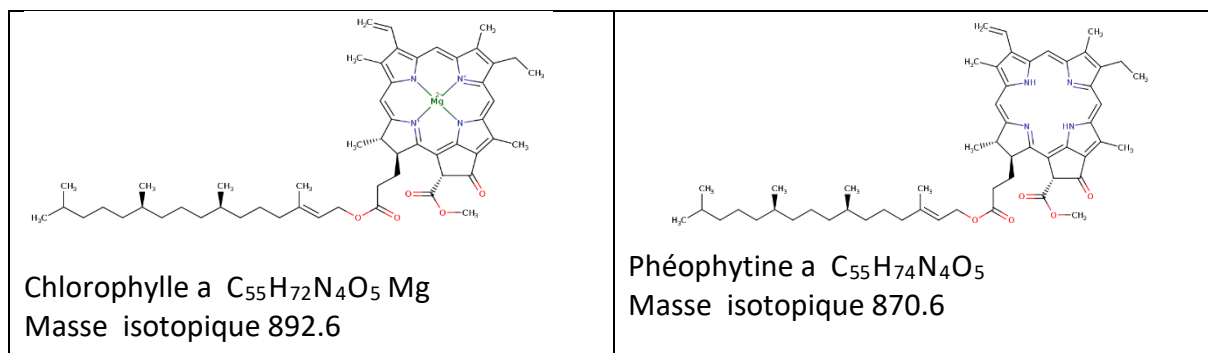
Magatte Diop<sup>1</sup>, Mosbah el-Hayek<sup>2</sup>, Satchin Soorkia<sup>1</sup>, Philippe Carbonnière<sup>3</sup>,  
Aurélien de la Lande<sup>2</sup>, Benoit Soep<sup>1</sup> et Niloufar Shafizadeh<sup>1</sup>

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Les Chlorophylles et leurs homologues les Phéophytines sont 2 pigments essentiels pour le processus de la photosynthèse. Il est bien connu que la Chlorophylle est une antenne très efficace pour absorber la lumière solaire. Puis l'énergie absorbée est transférée à un ensemble composé de quatre Chlorophylles et de deux Phéophytines au sein du système réactionnel 2 dit PSII. PSII est le siège d'une séparation de charge et in fine aboutit à la dissociation de l'eau.



Pour comprendre les propriétés de donneurs et accepteurs d'électrons de ces composés, nous avons étudié la Chlorophylle et la Phéophytine en mode positif et négatif par spectrométrie de masse. Sur ce poster on discutera de la stabilité des différents sites où se localisent les charges dans ces composés qui peuvent accepter ou donner un électron, en comparant les structures calculées aux résultats expérimentaux.

## Charge-carrier dynamics in CsPbBr<sub>3-y</sub>X<sub>y</sub>/TiO<sub>2</sub> (X = Cl, I) heterojunction at variable time scale

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Over the past decade, metal halide perovskites (MHP, CsPbX<sub>3</sub>: X = Cl, Br, I) have been widely investigated as promising materials for optoelectronics, achieving a record-breaking efficiency in solar cells.<sup>[1]</sup> From a fundamental point of view, MHP could be excellent candidates for photocatalysis due to their high photogenerated charge-carrier production and mobility as well as their narrow and tunable bandgap energy.<sup>[2]</sup> MHP with tuneable band-gap energy could be obtained through fast substitution of bromide by iodine or chloride (CsPbBr<sub>3-y</sub>X<sub>y</sub>: X = Cl, Br, I).<sup>[3]</sup>

In this work, we investigated charge-carrier dynamics of CsPbBr<sub>3-y</sub>X<sub>y</sub> along with interfacial electron transfer from CsPbBr<sub>3-y</sub>X<sub>y</sub> to TiO<sub>2</sub> by means of time resolved microwave conductivity (TRMC), time resolved photoluminescence (TRPL) and transient absorption spectroscopy (TAS). In order to find the optimal bandgap configuration for the most efficient charge injection, anionic ratio was varied. Charge-carrier injection from one material to another resulted in increased charge-carrier lifetime, which could positively affect the photocatalytic activity.

### Références

- [1] P. V. Kamat, *ACS Energy Lett.*, **4**, 1055–1056 (2009).
- [2] R. A. Scheidt, E. Kerns, P. V. Kamat, *J. Phys. Chem. Lett.*, **9**, 5962–5969 (2018).
- [3] G. Nedelcu, L. Protesescu, S. Yakunin, M. I. Bodnarchuk, M. J. Grotevent, M. V. Kovalenko, *Nano Lett.*, **15**, 5635–5640 (2015).

## **Spectroscopy and dynamics of NO photodonors**

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NO is highly unstable diatomic free radical. It has been shown to be both pro- and antitumorigenic, depending on the concentration and the given tumor microenvironment. Therefore, NO photodonors can be used to control the concentration of NO in-vivo and in specific sites for therapeutic applications. This work aims understanding the deactivation dynamics of excited electronic states and the mechanisms of photodissociation of specific NO photodonors which can be used as therapeutic agents.

The experimental setup comprises a ESI source, a temperature controlled clustering trap to generate hydrates and a cryogenic cold 3D quadrupole ion trap (QIT) to perform cryogenic ion photodissociation spectroscopy. The cold temperature achieved in the QIT (about 15 K) along with the set of available tunable lasers (IR/vis/UV) offer great opportunities for the precise studies of gas phase reaction of molecular ions, depending on their conformations, with a control of the excess energy deposited in the system and the detection of all the fragmentation channels. Multiple UV and IR photodissociation techniques have been developed, including single and double resonance spectroscopy on bare and hydrated nitrophenolate anionic species.



## Assessment of molecular origins of photobleaching of fluorescent proteins

Théo Beguin,<sup>1</sup> Frédéric Halgand,<sup>1</sup> Yasmina Bousmah, <sup>1</sup> H  l  ne Pasquier,<sup>1</sup> Marie Erard<sup>1</sup>

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Fluorescent Proteins are genetically encoded fluorescent probes that have become invaluable in bioscience/biophotonics as they allow the understanding of biological processes at the molecular level to get wonderful insights into living machines at work. The accurate monitoring of the biochemical event of interest deeply depends on their long term photostability, a poorly studied parameter until now. The improvement of the fluorescent protein photostability is a major challenge that requires a thorough understanding of the mechanisms involved in photobleaching.

Here, we report the first results of a study aimed at elucidating the mechanisms involved in the photobleaching of Citrine, a yellow-emitting fluorescent protein. Two experimental approaches have been used so far. On the one hand, the analysis of the evolution of the absorption spectra over the irradiation time allowed to propose a first simple kinetic model for photobleaching. On the other hand, the first results of mass spectroscopy provided initial information on the chemical nature of the generated photoproducts. A cleavage of the protein leading to the degradation of the chromophore was identified. In addition, the mass spectra showed mass additions, but also mass removals. The first results of the influence of the presence of oxygen are presented and discussed.



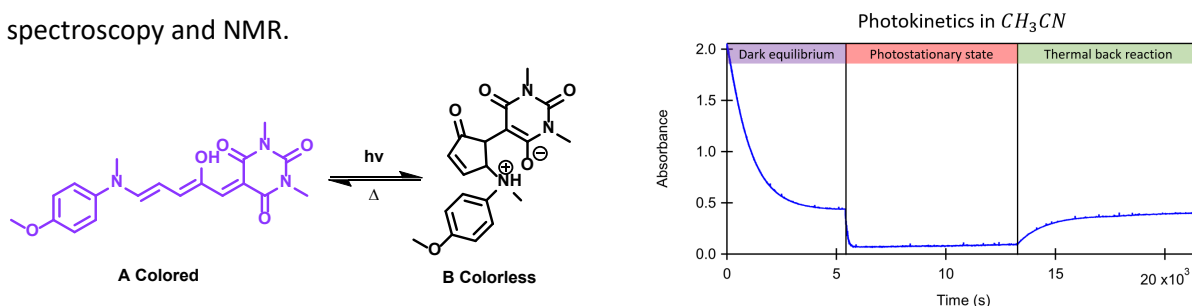
## Photophysical properties of negative photochromic compounds in solution

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Positive photochromic molecules are known and studied for decades<sup>[1], [2]</sup>. However, in the last few years, new families of photochromic molecules were discovered, for which the stable form A is colored and, thanks to irradiation with visible light, can be transformed into the colorless isomer B: this class of molecules is called “negative” photochromic compounds<sup>[3]</sup>. In this work, the properties of negative photochromic derivatives, belonging to the Donor-Acceptor Stenhouse Adducts (DASA) family, will be presented in solution (Figure 1, left)<sup>[4]</sup>. Steady-state spectroscopy was carried out in solution to provide the main spectral characteristics, whereas the continuous acquisition of absorption spectra in the presence or absence of illumination allows highlighting three major phenomena for the DASA compounds when dissolved in solution (Figure 1, right): a “dark equilibrium” which has been also followed by NMR, a “photostationary state” under irradiation, and a “thermal back reaction” in absence of light. Photophysical properties such as the conversion ratio, the quantum yield, and the kinetic rates can be extracted from photokinetics and the correlation between UV-vis absorption spectroscopy and NMR.



**Figure 1 :** (Left) Photochromic reaction of the DASA compound investigated in this work<sup>[4]</sup>. (Right) Photokinetic experiment showing the three distinct phenomena of a DASA in solution in the absence or presence of light (absorbance is measured at 580 nm, in the absorption band of the colored form, irradiation is carried out at 575 nm).

<sup>[1]</sup> K. Nakatani, J. Piard, P. Yu, R. Métivier, *Introduction: organic photochromic molecules, in Photochromic materials: preparation, properties and applications, 1st ed. (Eds.: H. Tian, J. Zhang), Wiley-VCH, 2016, pp. 1-45.*

<sup>[2]</sup> H. Dürr, H. Bouas-Laurent (ed), *Photochromism, Molecules, and Systems, Elsevier, Amsterdam, 1990, 1068 pages.*

<sup>[3]</sup> M. M. Lerch, W. Szymanski, B. L. Feringa, *The (photo)chemistry of Stenhouse photoswitches: guiding principles and system design, Chem. Soc. Rev. 2018, 47, 1910-1937.*

<sup>[4]</sup> N. Mallo, E. D. Foley, H. Iranmanesh, A. D. W. Kennedy, E. T. Luis, J. Ho, J. B. Harper, J. E. Beves, *Structure-function relationships of donor-acceptor Stenhouse adduct photochromic switches, Chem. Sci. 2018, 9, 8242-8252.*

**Complex sulfation pattern observed in glycosaminoglycan sequences deciphered by hydrophilic interaction liquid chromatography-mass spectrometry.**

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Glycosaminoglycans (GAGs) are anionic polysaccharides involved in physiological and pathological processes such as cerebral plasticity and mucopolysaccharidosis [1]. GAGs constitute one of the dominant components of the extracellular matrix through which the communications necessary for biological and physical interactions between cells are carried out. GAG chains are composed of disaccharide repeating units consisting of an hexuronic acid and a hexosamine. These disaccharides can be modified at multiple positions by sulfation, acetylation, and epimerization, creating isomeric heterogeneity that makes their sequence identification a real analytical challenge. Interaction of GAGs with different biological factors has raised a great interest in their use in drug development by establishing the structure-function relationship of GAGs is a significant challenge due to their broad diversification of structure.

Advances in mass spectrometry (MS) and hydrophilic interaction liquid chromatography (HILIC) techniques have prompted considerable progress in the structural characterization of GAGs [2, 3]. However, due to the fragile nature of their sulfate groups, their structural elucidation remains a challenge in tandem mass spectrometric analysis (MS/MS). In this study, our goal was to distinguish GAGs isomers of different nature (heparin and chondroitin sulfate for instance) and polymerization degrees in complex matrix. The development of HILIC-MS/MS techniques allowed us to distinguish by HILIC and identify by MS/MS disaccharide isomers of both heparin and chondroitin sulfate analogues in less than 30 minutes. However, oligosaccharides of higher polymerization degrees (DP) remain difficult to distinguish using this 2D methodology. To circumvent this limitation, the behavior of these different isomers was studied by ion mobility mass spectrometry (IMS-MS) and allowed us to distinguished carboxylic acid orientation isomers of oligosaccharides up to DP 12. This methodology was applied to monitor *in situ* different enzymatic reactions on their natural oligosaccharide substracts.

#### Références

- [1] S. Ricard-Blum et al. *Glycoconj. J.*, 34, 339-349 (2017).
- [2] S. Poyer et al. *Rapid Commun. Mass Spectrom.*, 31, 2003-2010 (2017).
- [3] S. Poyer et al. *Anal. Bioanal. Chem.*, 413, 7107-7117 (2021).

## Coarse-grained modelling of DNA translocation through a protein nanopore

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Molecular-scale nanopores are discovered to be strong candidates for detection at single molecule level, due to their intrinsic sensing properties. Recent studies have demonstrated their potential for nanoscale detection in various fields of biology, biophysics, biotechnology and nanotechnology [1, 6]. Nanopore technology is therefore regarded as a powerful and precise method for single-molecule sensing, among which DNA sequencing has received a great research interest and is proving to be successful [3]. However, the dynamics of DNA sequencing through protein nanopores remains insufficiently explored. Our aim is to understand the molecular details of DNA translocation through  $\alpha$ -hemolysin ( $\alpha$ HL) nanopore, a broadly-used nanopore [2], using coarse-grained (CG) molecular dynamics (MD) simulations. The MARTINI force-field [4, 5] was used for all CG-MD simulations and our system is composed of an  $\alpha$ HL nanopore, a lipid membrane, a single stranded DNA (ssDNA) molecule in 1M ionic solution, (500,000 atoms, 140,000 CG beads). In order to study in detail the translocation process as a function of DNA length and direction at the nanopore entry, several systems with different ssDNA lengths and orientations were prepared and simulated for 500 ns using steered MD to drive the DNA through the nanopore. Our preliminary results shed light on the dynamics of driven translocation of DNA through  $\alpha$ HL nanopore with the aim of developing efficient detection devices.

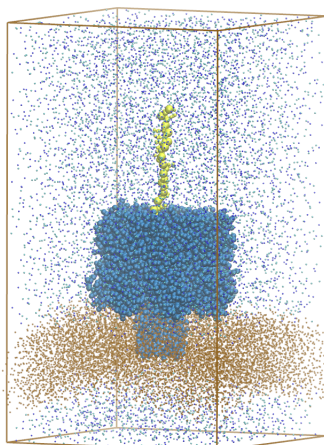


Figure 1: Coarse-grained representation of the system.

### References

- [1] F. Bošković and U. F. Keyser. Toward single-molecule proteomics. *Science*, 374(6574):1443–1444, Dec 2021.
- [2] G. Di Muccio, A. E. Rossini, D. Di Marino, G. Zollo, and M. Chinappi. Insights into protein sequencing with an  $\alpha$ -hemolysin nanopore by atomistic simulations. *Scientific Reports*, 9(1):6440, Apr 2019.
- [3] M. Jain, S. Koren, K. H. Miga, J. Quick, A. C. Rand, T. A. Sasani, J. R. Tyson, A. D. Beggs, A. T. Dilthey, I. T. Fiddes, S. Malla, H. Marriott, T. Nieto, J. O’Grady, H. E. Olsen, B. S. Pedersen, A. Rhie, H. Richardson, A. R. Quinlan, T. P. Snutch, L. Tee, B. Paten, A. M. Phillippy, J. T. Simpson, N. J. Loman, and M. Loose. Nanopore sequencing and assembly of a human genome with ultra-long reads. *Nature Biotechnology*, 36(4):338–345, Apr 2018.
- [4] L. Monticelli, S. K. Kandasamy, X. Periole, R. G. Larson, D. P. Tieleman, and S.-J. Marrink. The martini coarse-grained force field: Extension to proteins. *Journal of Chemical Theory and Computation*, 4(5):819–834, Apr 2008.
- [5] J. J. Uusitalo, H. I. Ingólfsson, P. Akhshi, D. P. Tieleman, and S. J. Marrink. Martini coarse-grained force field: Extension to dna. *Journal of Chemical Theory and Computation*, 11(8):3932–3945, Jul 2015.
- [6] E. C. Yusko, B. R. Bruhn, O. M. Eggenberger, J. Houghtaling, R. C. Rollings, N. C. Walsh, S. Nandivada, M. Pindrus, A. R. Hall, D. Sept, J. Li, D. S. Kalonia, and M. Mayer. Real-time shape approximation and fingerprinting of single proteins using a nanopore. *Nat Nanotechnol*, 12(4):360–367, Dec. 2016.

**FRET-FLIM imaging, a powerful technique to explore protein-protein interactions at the endoplasmic reticulum membrane**

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The Endoplasmic Reticulum (ER) is a highly dynamic organelle that continuously forms contacts with other cellular compartments at Membrane Contact Sites (MCS). Several proteins are involved in their formation and in the signaling processes located at MCSs. The study of these MCSs is a relatively recent undertaking, and much about them is still unknown. Numerous protein interactions are still unidentified, and their molecular organization is inaccessible to date.

We developed a FRET-FLIM imaging strategy to study MCSs. We used fluorescent proteins (FPs)-tagged members of membrane-bound proteins known to form MCS. We focused on three protein families: The E-SYTs, VAPs, and ORPs. The FPs' FRET pair was chosen for their brightness, photostability, and their ability to be monomeric. From our FLIM data, we can characterize molecular interactions and quantify their relative intensities within the complexes.

Our preliminary results showed (1) that E-SYTs, VAPs, and ORPs form oligomers within their families, (2) there is no interaction between E-SYT1 and ORPs, and (3) VAPs are in close proximity with ESYTs and ORPs but may not oligomerize.

Our future goal is to further develop this method to differentiate between oligomerization and close contacts due to microdomains in the ER membrane. We will also adapt our FRET-FLIM strategy for the space and time tracking of MCSs.

## Ferroelectric system for photoelectrochemical water oxidation

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Photoelectrocatalysis, as a powerful tool, can be used for energy conversion and environmental redemption.<sup>1</sup> However, current photoelectrocatalytic efficiency of the semiconductors is largely limited by the effective separation of photogenerated charge-carriers.<sup>2</sup> The introduction of a built-in electric field induced by polarization of ferroelectric materials is an efficient way to modulate the migration behavior of photogenerated charge-carriers.<sup>3,4</sup> In this work, a BaTiO<sub>3</sub>@TiO<sub>2</sub> ferroelectric system has been proposed for higher photoelectrocatalytic performance. To better understand the effect of ferroelectric polarization on the photoelectrocatalytic performance of this ferroelectric system, the polarization state of BaTiO<sub>3</sub> has been manipulated by crystalline phases and electric poling directions. The obtained ferroelectric system was characterized by XRD, SEM, EDX, UV-Vis Spectra, and Time Resolved microwave conductivity (TRMC) to ascertain the structure and electronic properties of the composites. The difference in photoelectrocatalytic reactivity of these samples was investigated through photoelectrochemical (PEC) test. This work will provide a promising strategy to design high performance photoelectrochemical systems.

### Références

- [1] L. Jing et al. Chem. Soc. Rev. **42**, 9509 (2013).
- [2] C. Ding et al. ACS Catalysis, **7**, 675 (2016).
- [3] F. Wu et al. Adv. Mater. **29**, 1701432 (2017).
- [4] M. Zhang et al. Nano Energy, **81**, 105626 (2021).

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